Defending the Rights of Metals:

How to Distinguish Naturally High Groundwater Concentrations from Site-Related Contamination

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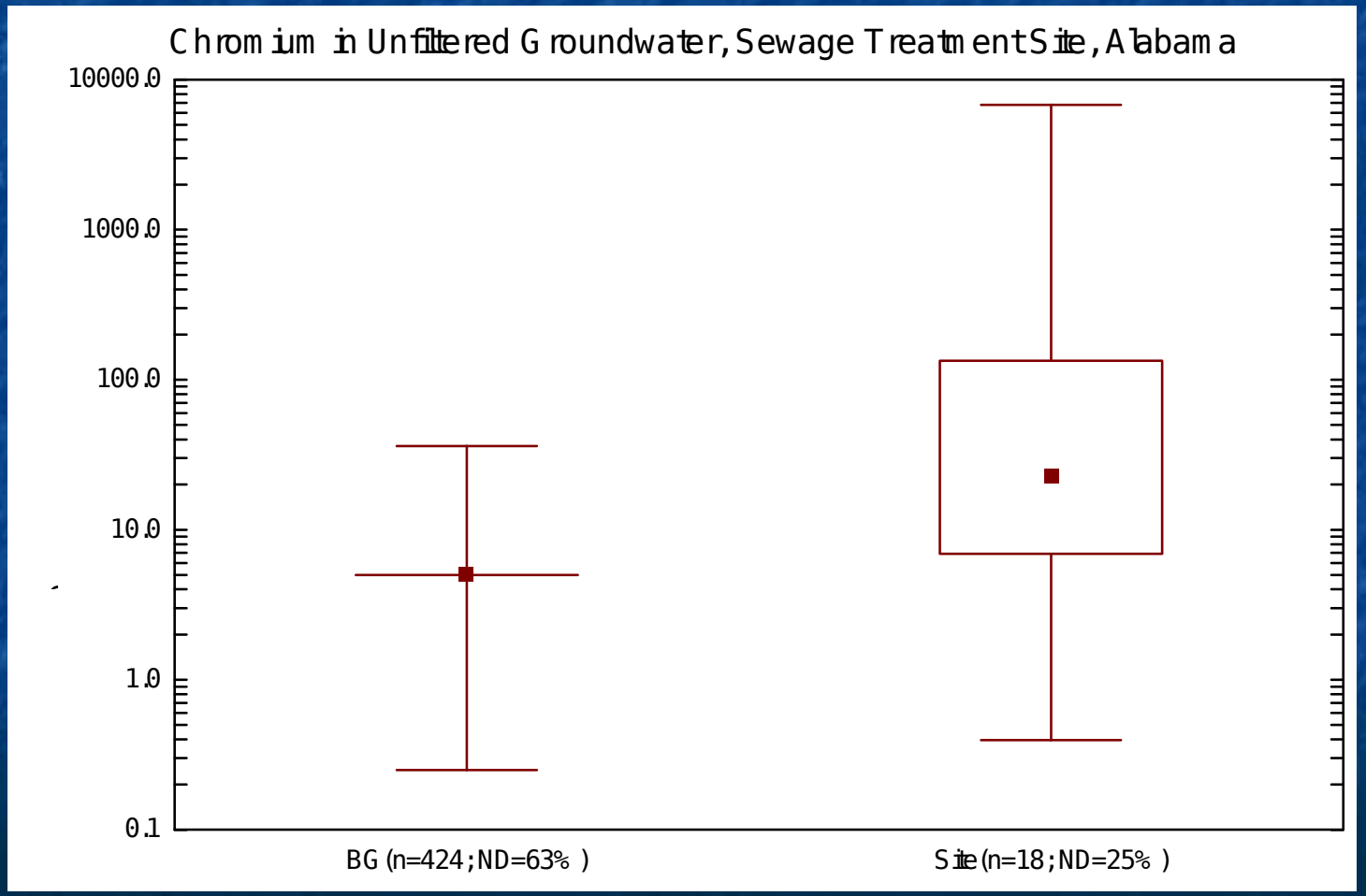
Typical Definitions of Metals Contamination in Groundwater

- Concentrations that exceed MCLs
- Concentrations that exceed risk-based screening levels
- Concentrations that exceed background screening values, or fail other statistical comparisons to background data sets

Typical Definitions of Metals Contamination in Groundwater



Problems With These Standard Approaches

- Trace elements in groundwater can have naturally large ranges (3 to 4 orders of magnitude)
- Distributions are highly skewed (lognormal)
- Insufficient number of background samples
- Unequal sample sizes (site [n] >> background [m])
- Geochemical processes are ignored

...Unnecessary monitoring, risk assessment, or remediation can ensue if metals in site groundwater are erroneously identified as contaminants.

Geochemical evaluation should be performed to properly distinguish actual contamination from naturally high background.

Reasons for Elevated Metals Concentrations in Groundwater

- Suspended particulates
- Reductive dissolution
- pH effects
- Contamination

Effects of Suspended Particulates

- Most common suspended particulates in groundwater are clay minerals, hydrous aluminum oxides, aluminum hydroxides; and iron oxides, iron hydroxides, iron oxyhydroxides
- In neutral-pH water, Al concentrations > 1 mg/L indicate suspended Al-bearing minerals (clays)

  (–) *surface charge*
- In neutral-pH, moderate to oxidizing redox conditions, Fe concentrations > 1 mg/L indicate suspended iron oxides

  (+) *surface charge*

Effects of Suspended Particulates

- Trace elements are associated with specific suspended particulates, yielding good correlations for trace-vs.-reference element concentrations in uncontaminated samples
- Oxyanionic elements – negatively charged speciation under oxidizing conditions

Arsenic (V):	$HAsO_4^{2-}$, $H_2AsO_4^-$	Iron oxides (Fe)
Antimony (V):	$Sb(OH)_6^-$	
Selenium (VI):	SeO_4^{2-}	
Vanadium (V):	$H_2VO_4^-$, HVO_4^{2-}	

Effects of Suspended Particulates

- Cationic elements – positively charged speciation

Barium: Ba^{2+}
Lead: Pb^{2+}
Nickel: Ni^{2+}
Zinc: Zn^{2+}

} Clays (Al) and/or manganese oxides (Mn)

- Mixed elements – multiple charges at equilibrium

Chromium (III): $Cr(OH)_2^+$, $Cr(OH)_3^o$, $Cr(OH)_4^-$

Effects of Reductive Dissolution

- Releases of organic contaminants (fuel, solvents) can establish local reducing environments via anaerobic microbial activity
- These conditions drive the dissolution of iron oxides and manganese oxides, thereby mobilizing trace elements that were adsorbed on the oxide surfaces

Effects of Reductive Dissolution

- Identified by correlations of metals with indicators of local redox depression:

  Low ORP and DO

  Elevated dissolved Fe and Mn

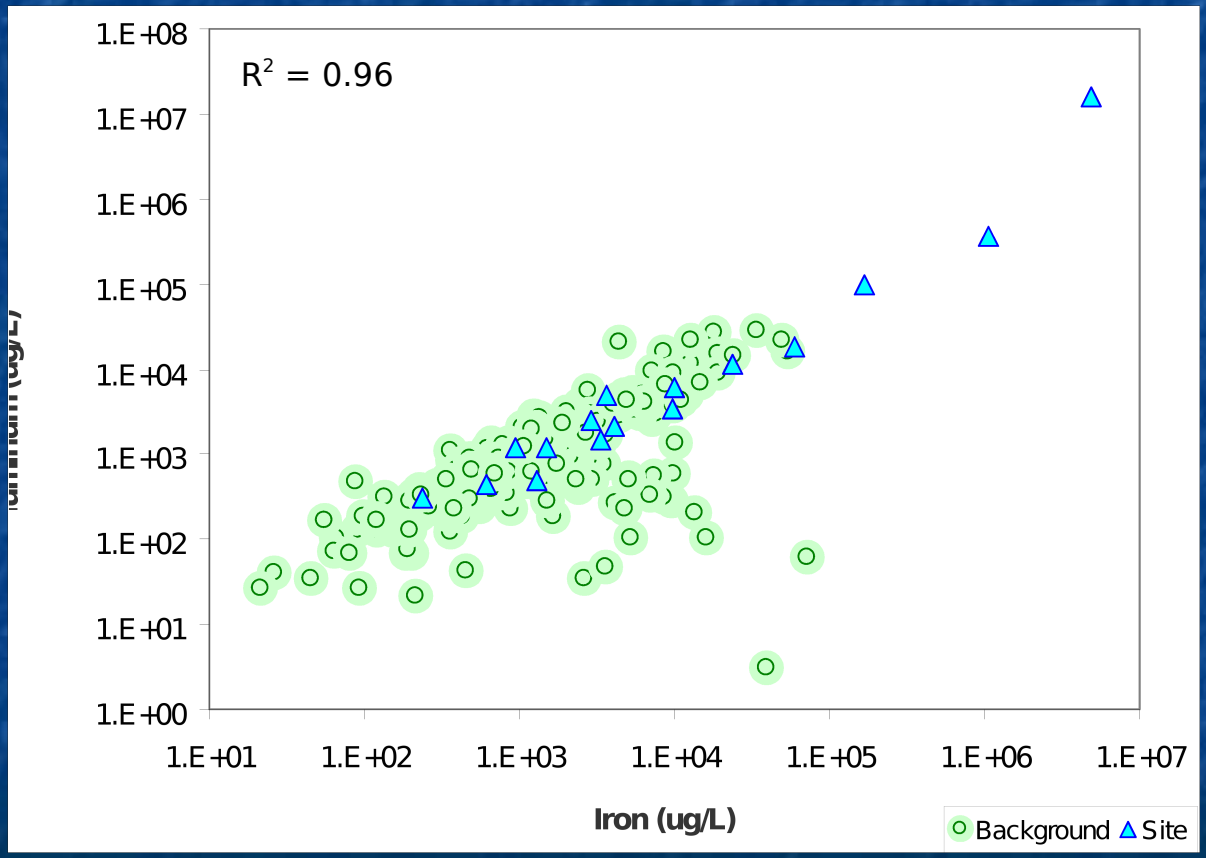
  Lower sulfate and nitrate

  Detectable sulfide and ammonia

  Detectable hydrogen, methane, ethene, ethane

  Anaerobic Cl-solvent degradation products (*cis*-1,2-DCE, vinyl chloride)

Site 1 (Alabama): Aluminum vs. Iron in Unfiltered Groundwater



n = 16 (m = 300)

pH: 4.9 to 8.3

mean = 6.6

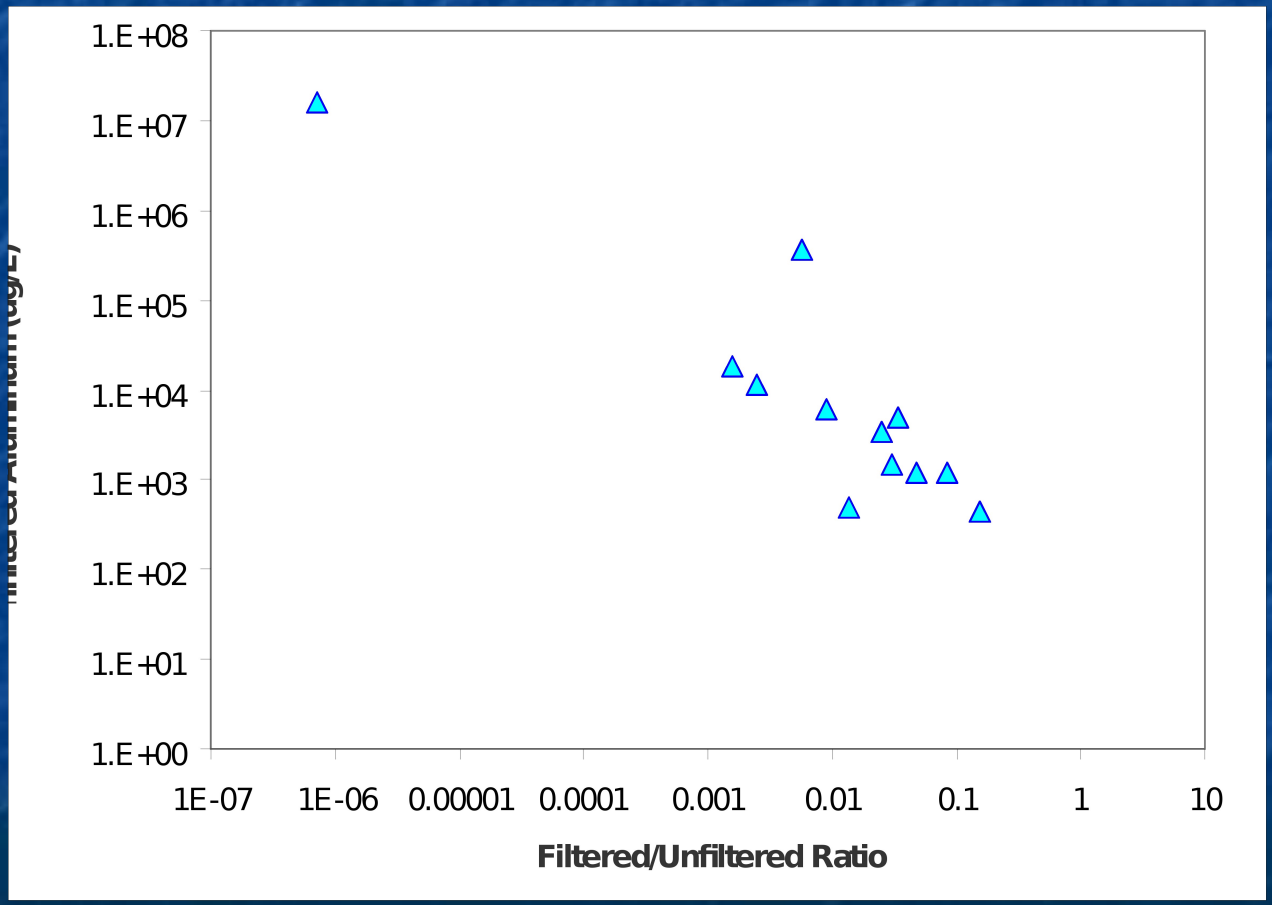
DO: 1.1 to 6.9 mg/L

mean = 5.2 mg/L

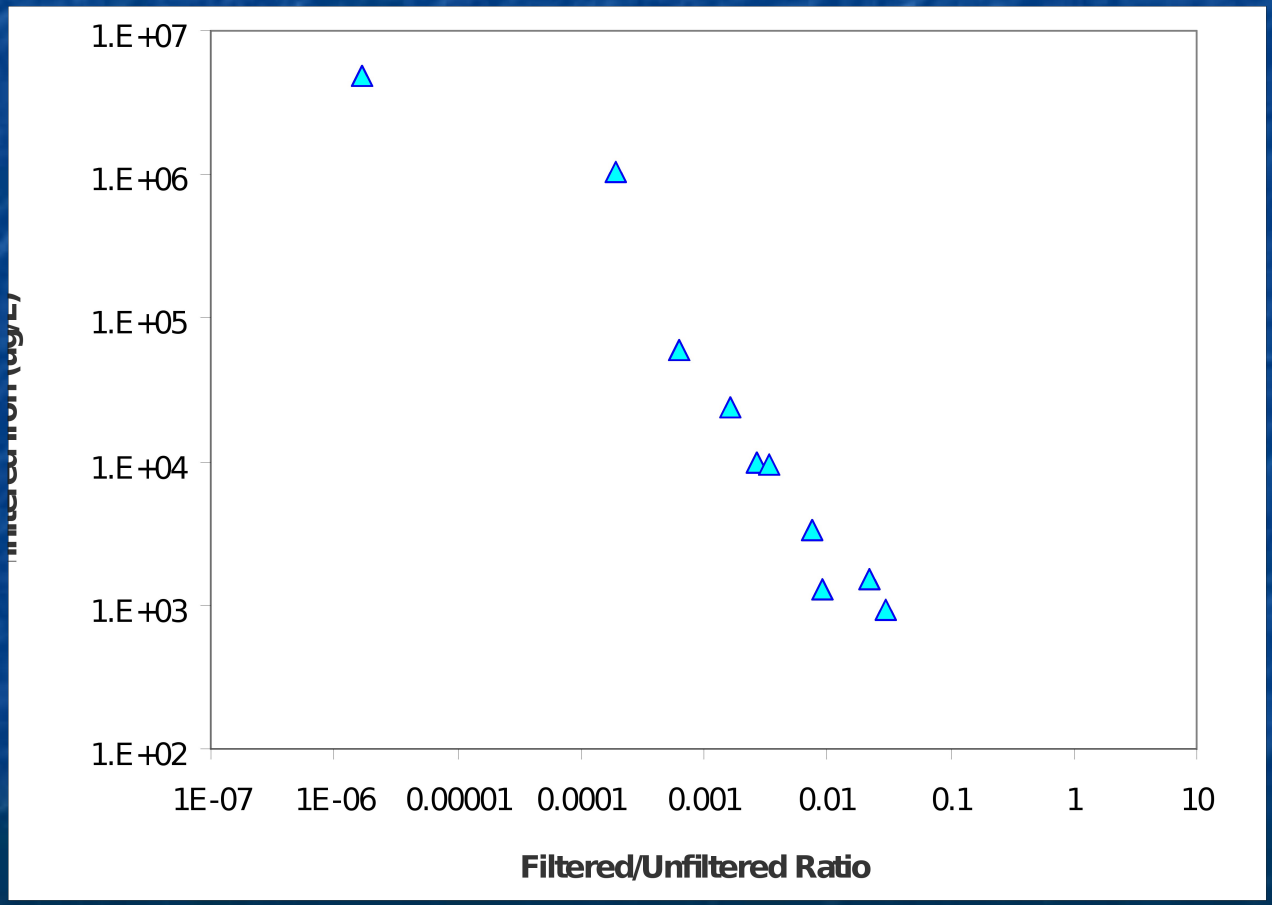
ORP: +148 to +272 mV

mean = +212 mV

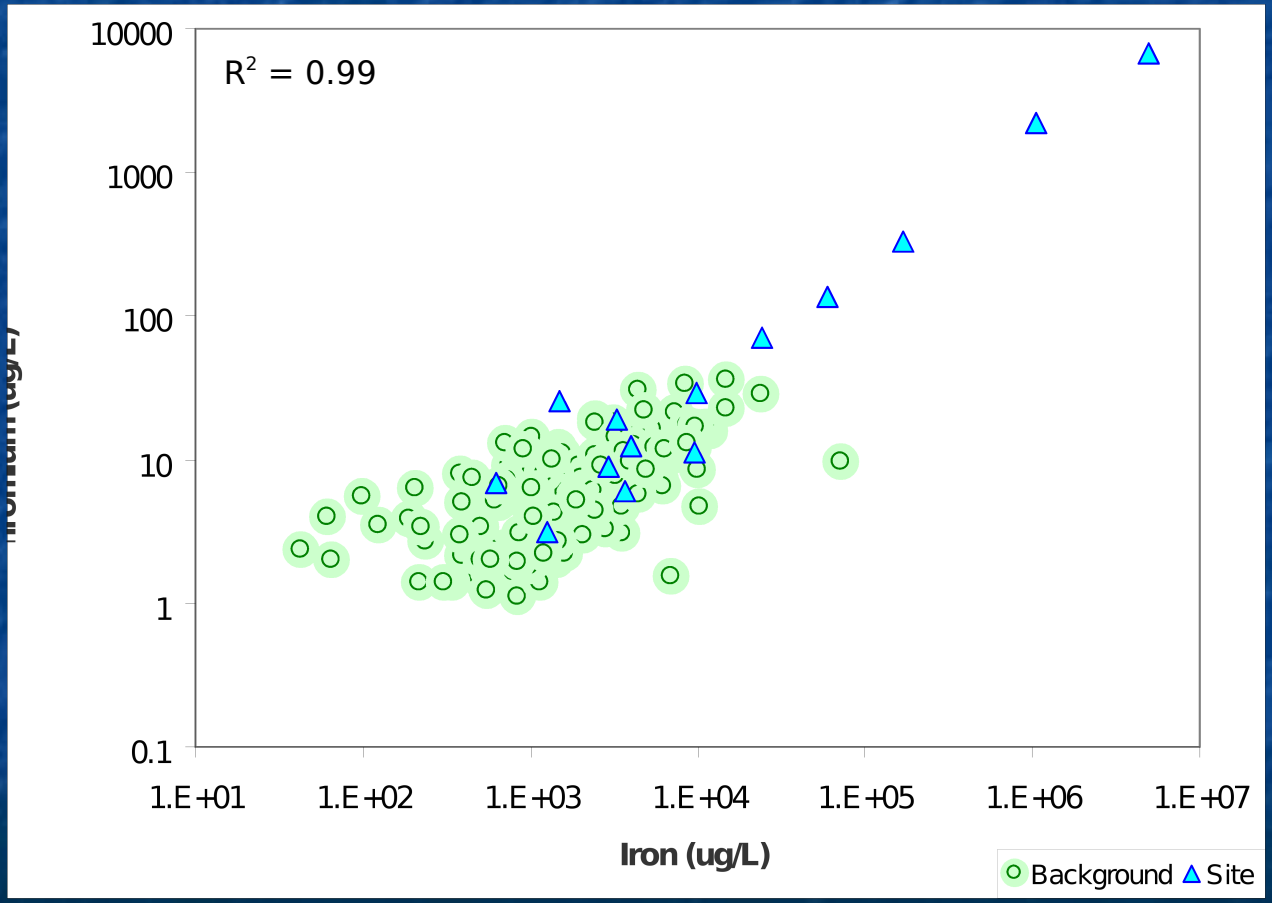
Site 1 (Alabama): Unfiltered Aluminum vs. Filtered/Unfiltered Ratio



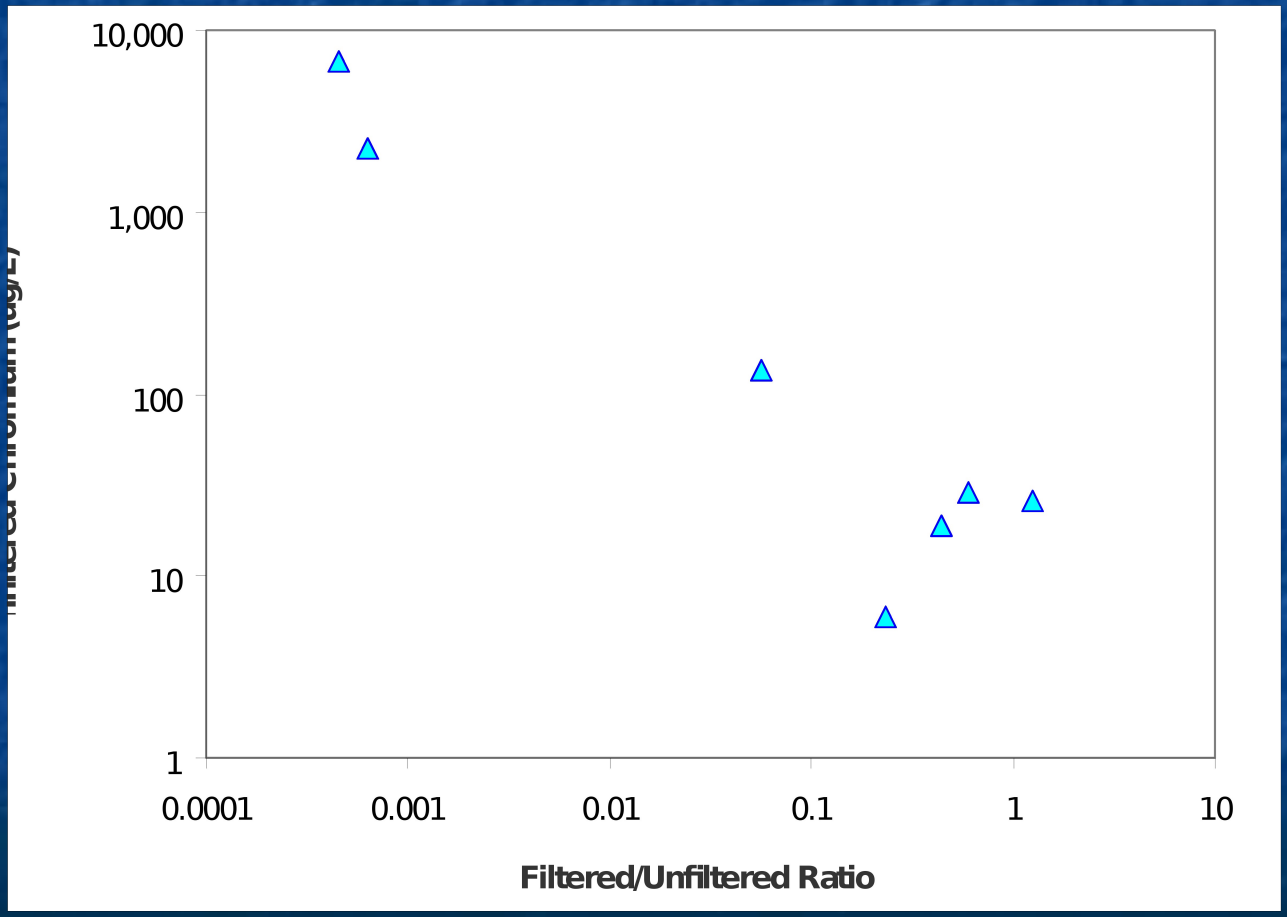
Site 1 (Alabama): Unfiltered Iron vs. Filtered/Unfiltered Ratio



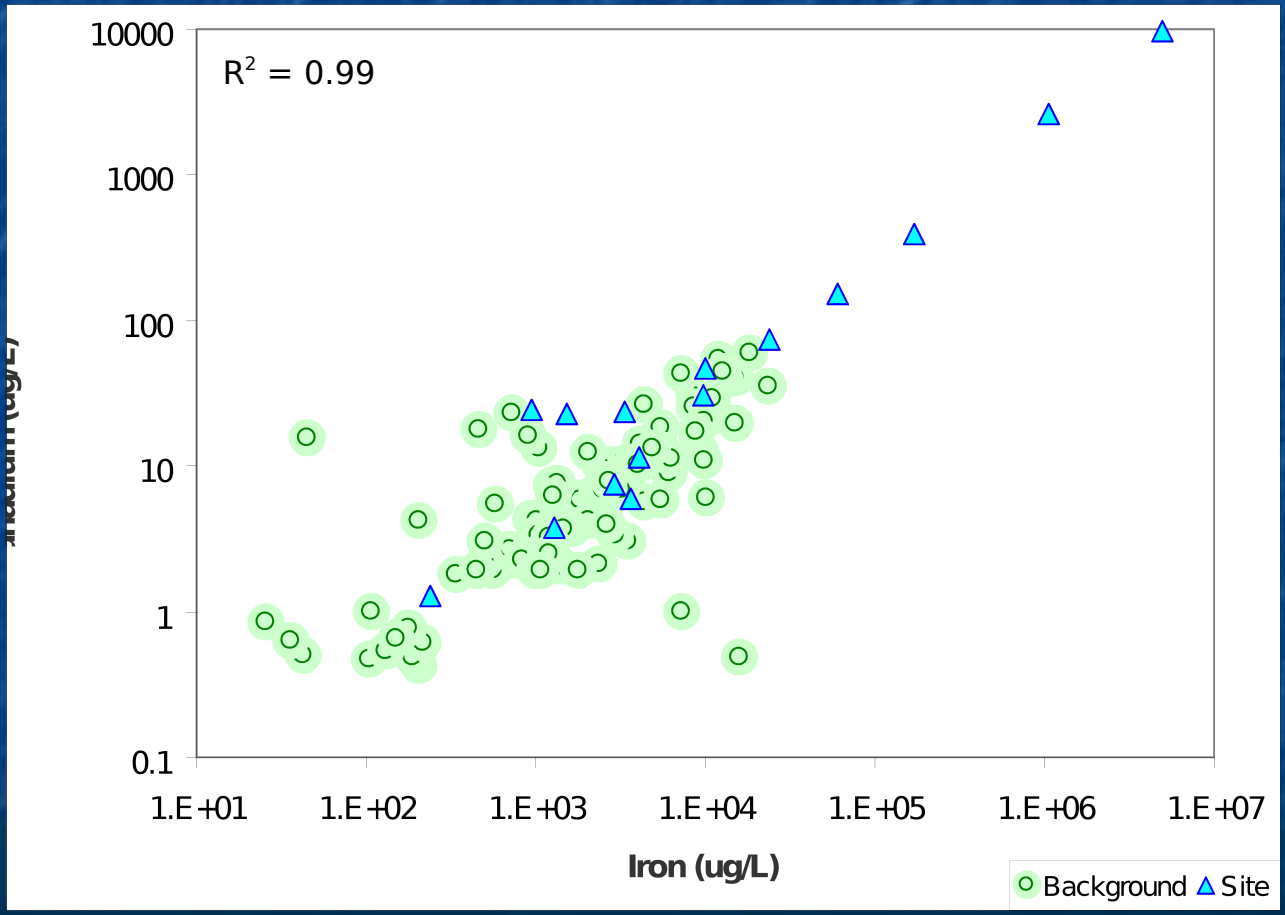
Site 1 (Alabama): Chromium vs. Iron in Unfiltered Groundwater



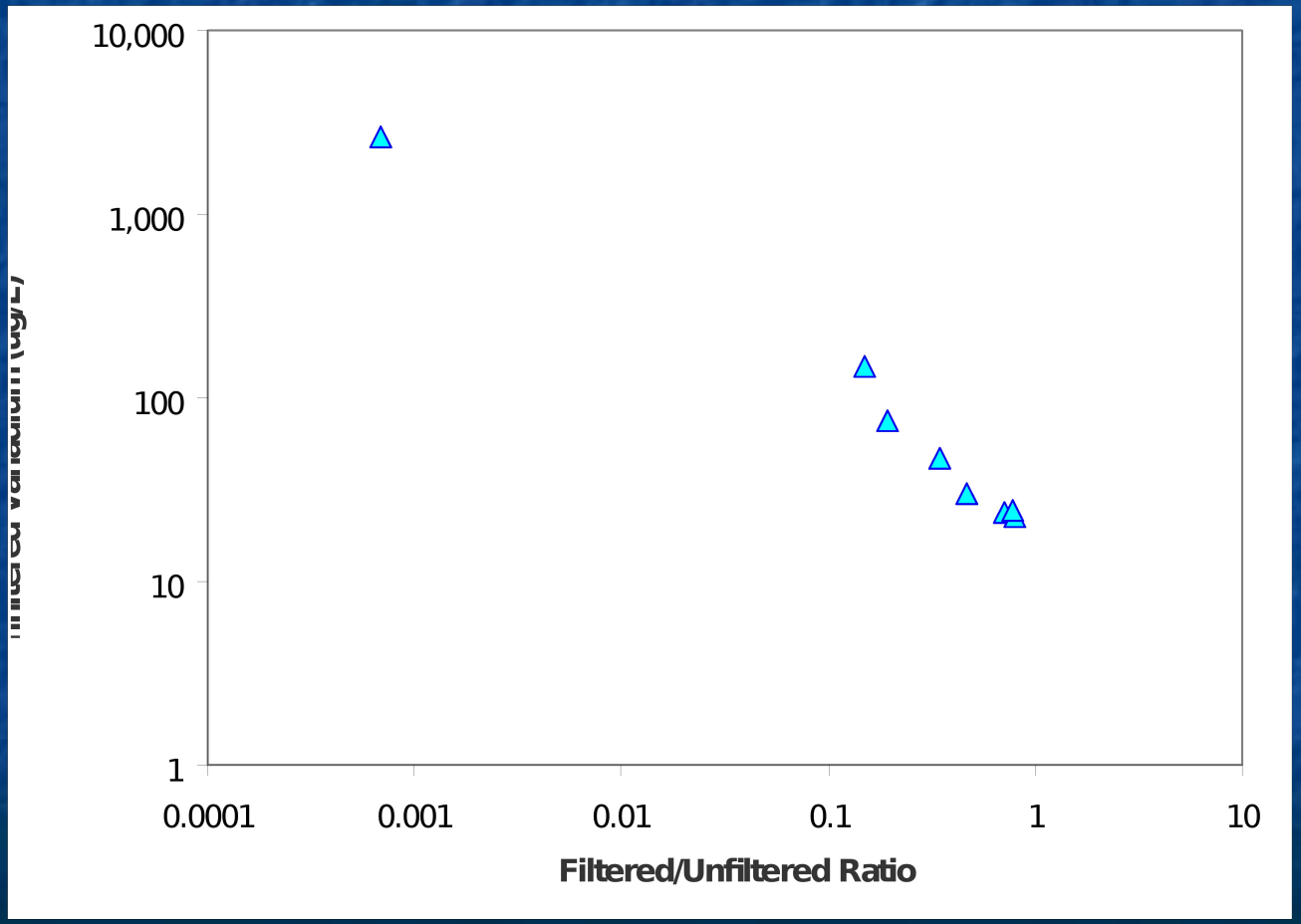
Site 1 (Alabama): Unfiltered Chromium vs. Filtered/Unfiltered Ratio



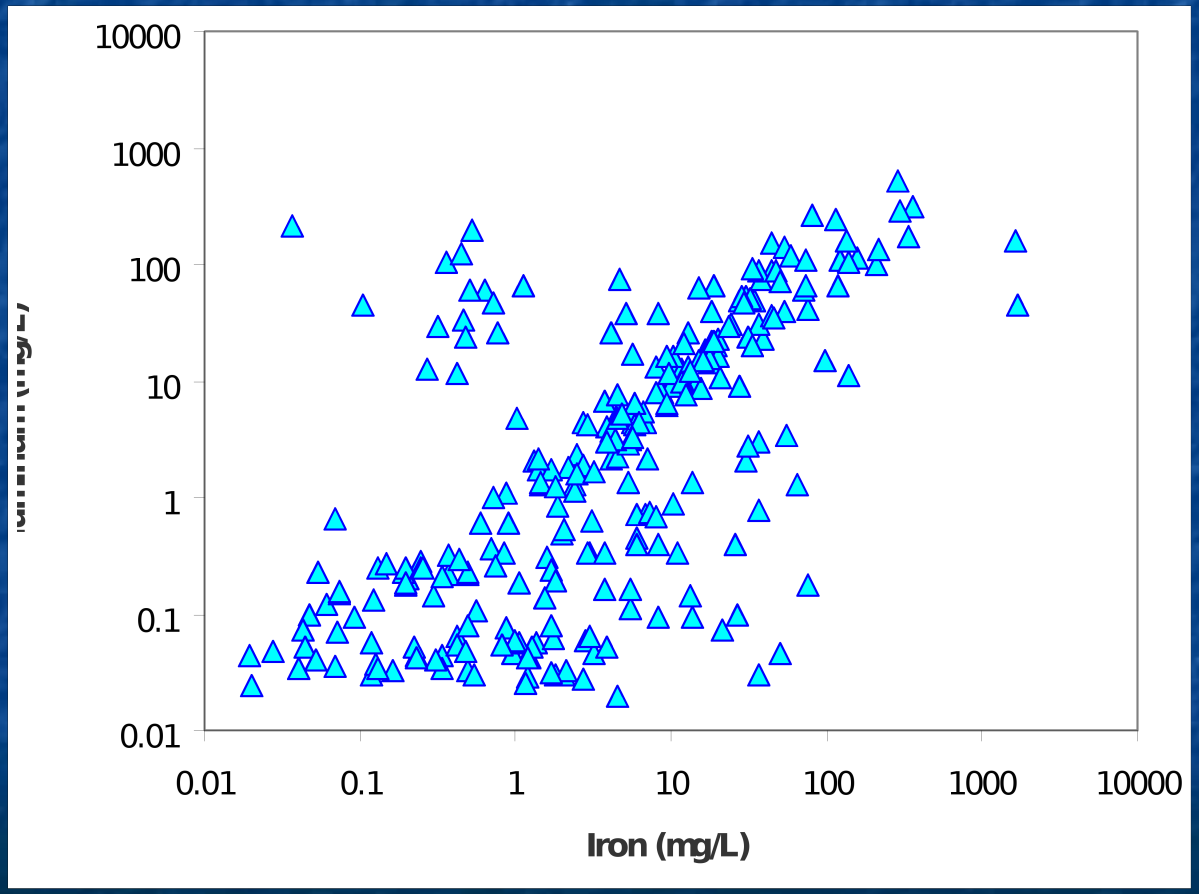
Site 1 (Alabama): Vanadium vs. Iron in Unfiltered Groundwater



Site 1 (Alabama): Unfiltered Vanadium vs. Filtered/Unfiltered Ratio



Site 2 (Georgia): Aluminum vs. Iron in Unfiltered Groundwater



n = 352

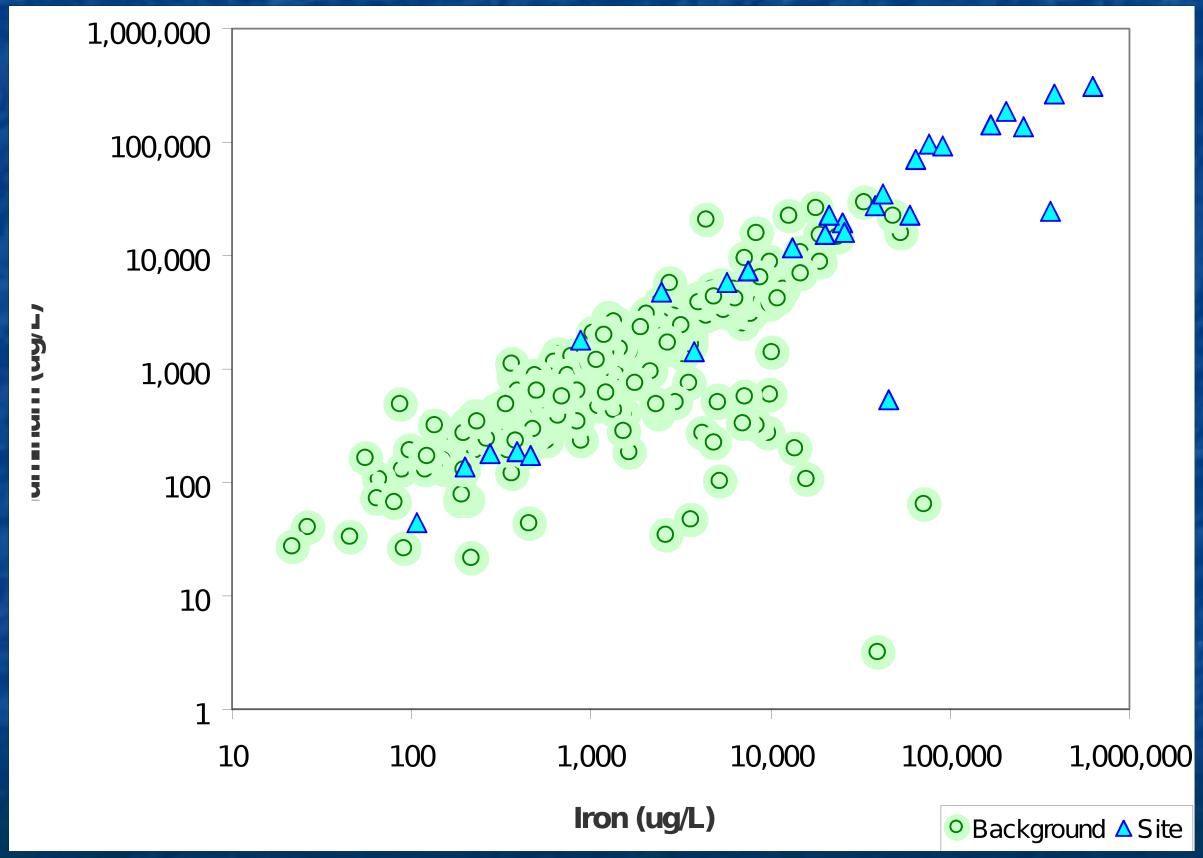
pH: 4.3 to 8.4

mean = 5.9

DO: 1.3 to 12.6 mg/L

mean = 8.4 mg/L

Site 3 (Alabama): Aluminum vs. Iron in Unfiltered Groundwater



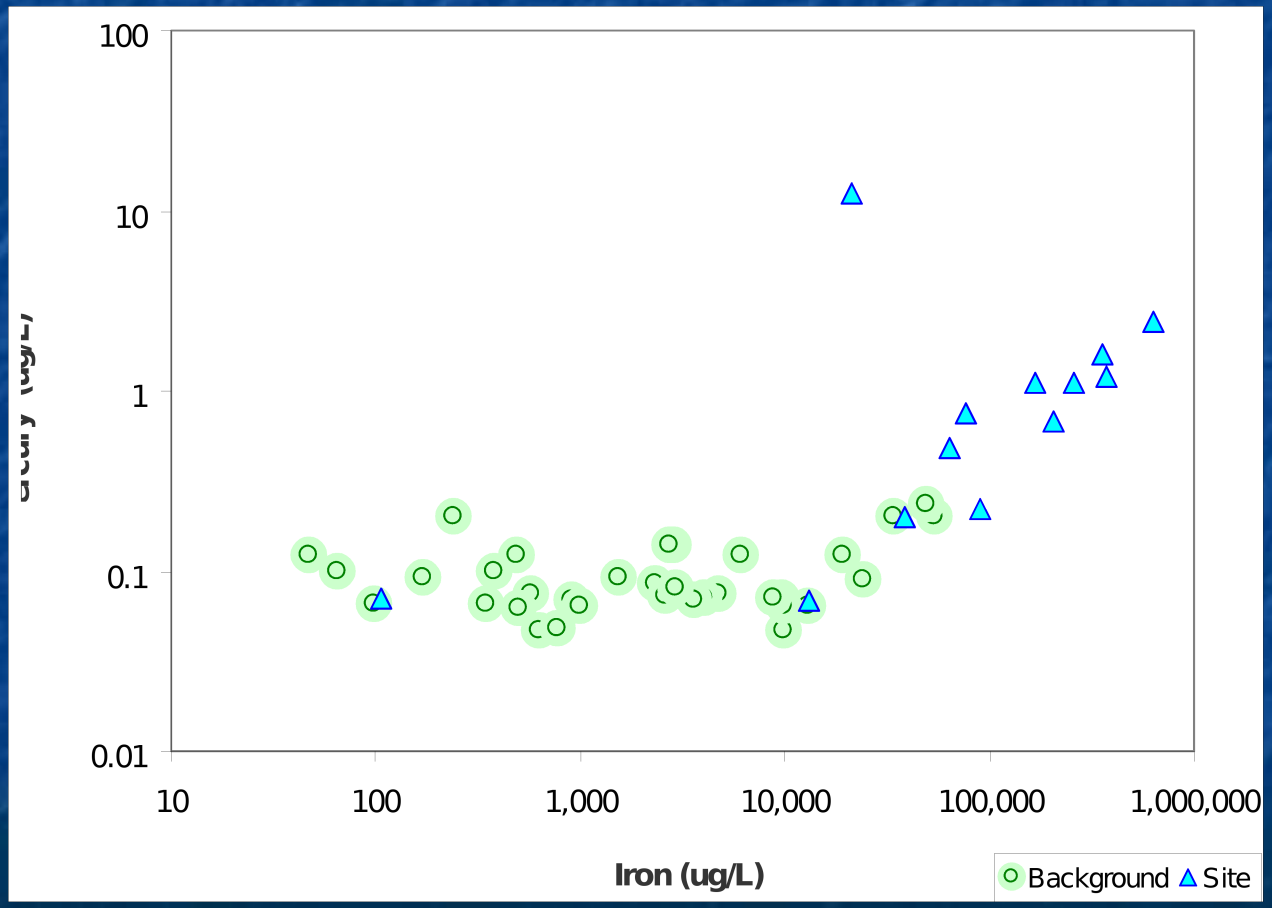
n = 30 (m = 300)

pH: 5.8 to 6.2

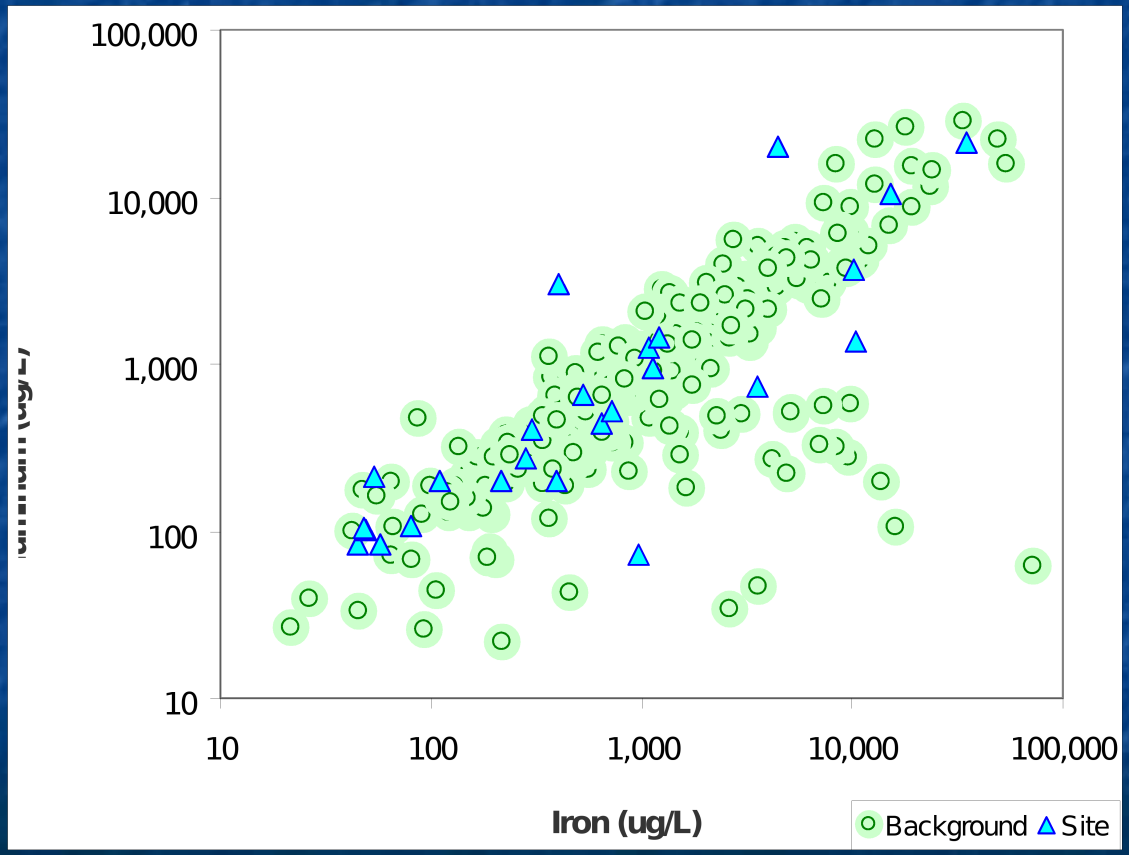
DO: 0.9 to 10.4 mg/L

ORP: -210 to +82 mV

Site 3 (Alabama): Mercury vs. Iron in Unfiltered Groundwater



Site 4 (Alabama): Aluminum vs. Iron in Unfiltered Groundwater



n = 43 (m = 300)

pH: 5.0 to 12.7

mean = 7.7

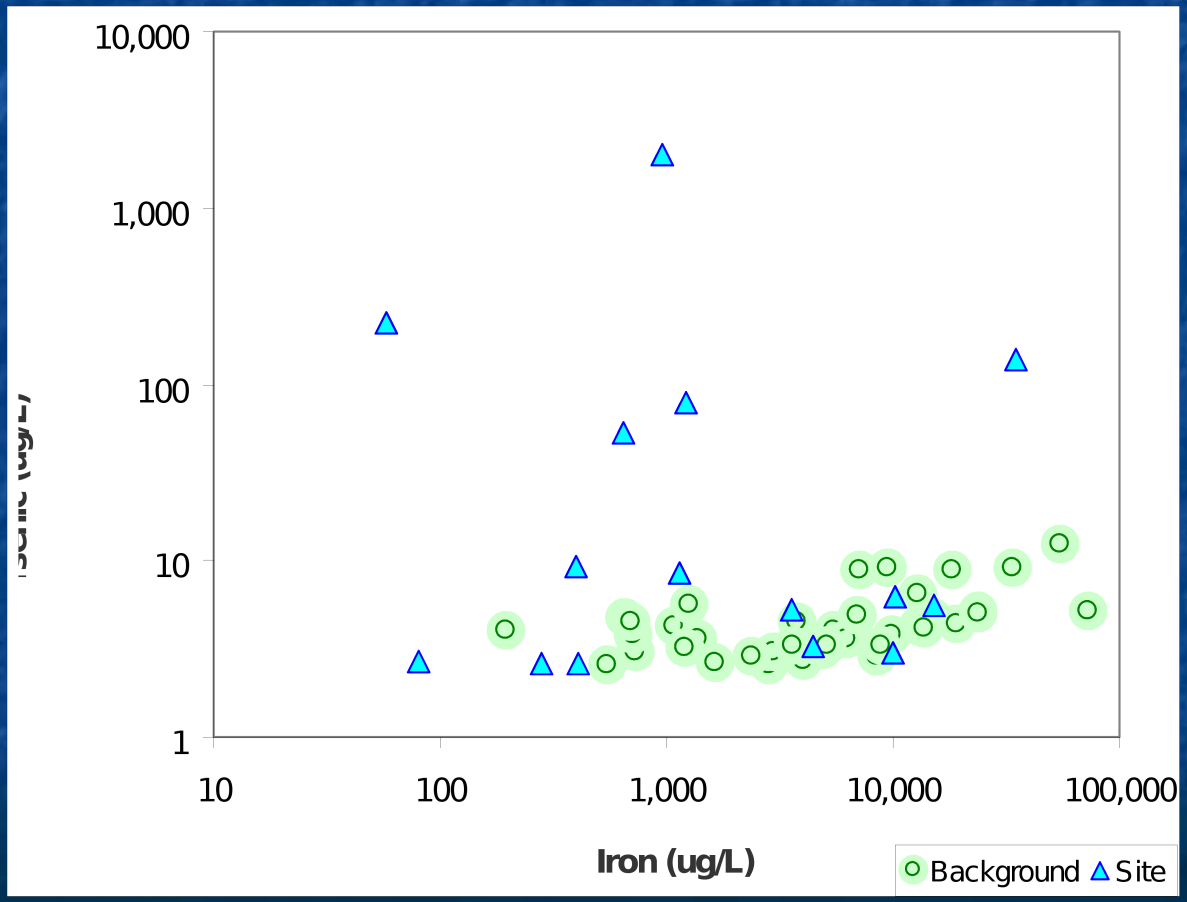
DO: 0.7 to 5.7 mg/L

mean = 3.0 mg/L

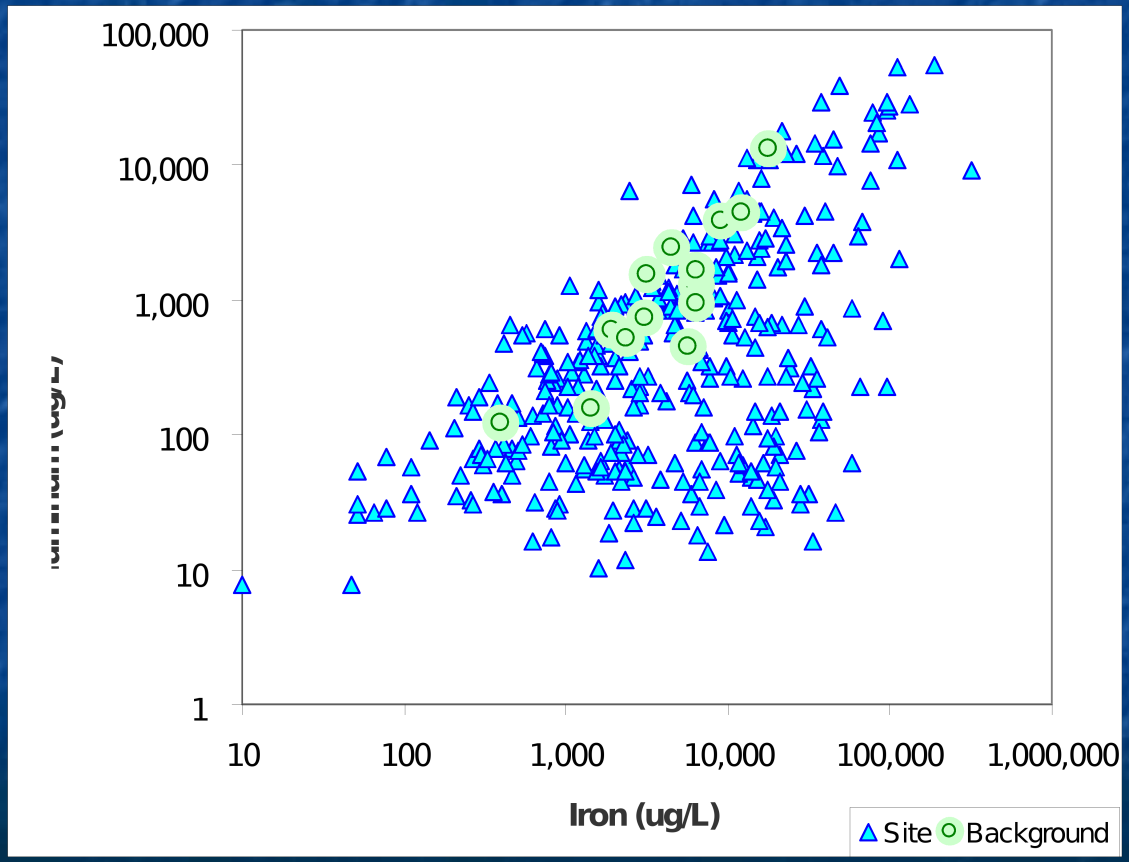
ORP: -270 to +268 mV

mean = +104 mV

Site 4 (Alabama): Arsenic vs. Iron in Unfiltered Groundwater



Site 5 (Virginia): Aluminum vs. Iron in Unfiltered Groundwater



n = 407 (m = 11)

TDS: 153 to 25,800 mg/L

mean = 4,350 mg/L

pH: 4.9 to 10.6

mean = 7.0

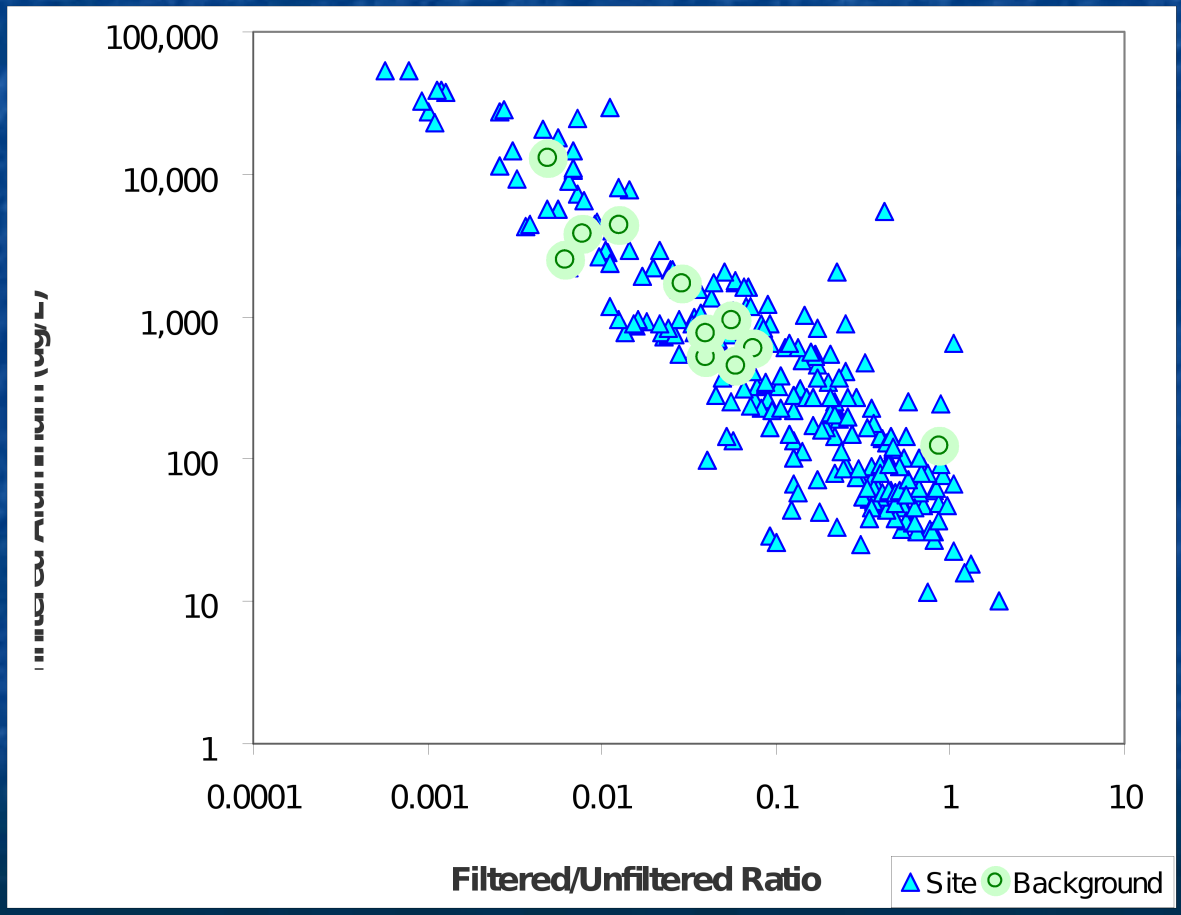
DO: 0.1 to 13.6 mg/L

mean = 5.1 mg/L

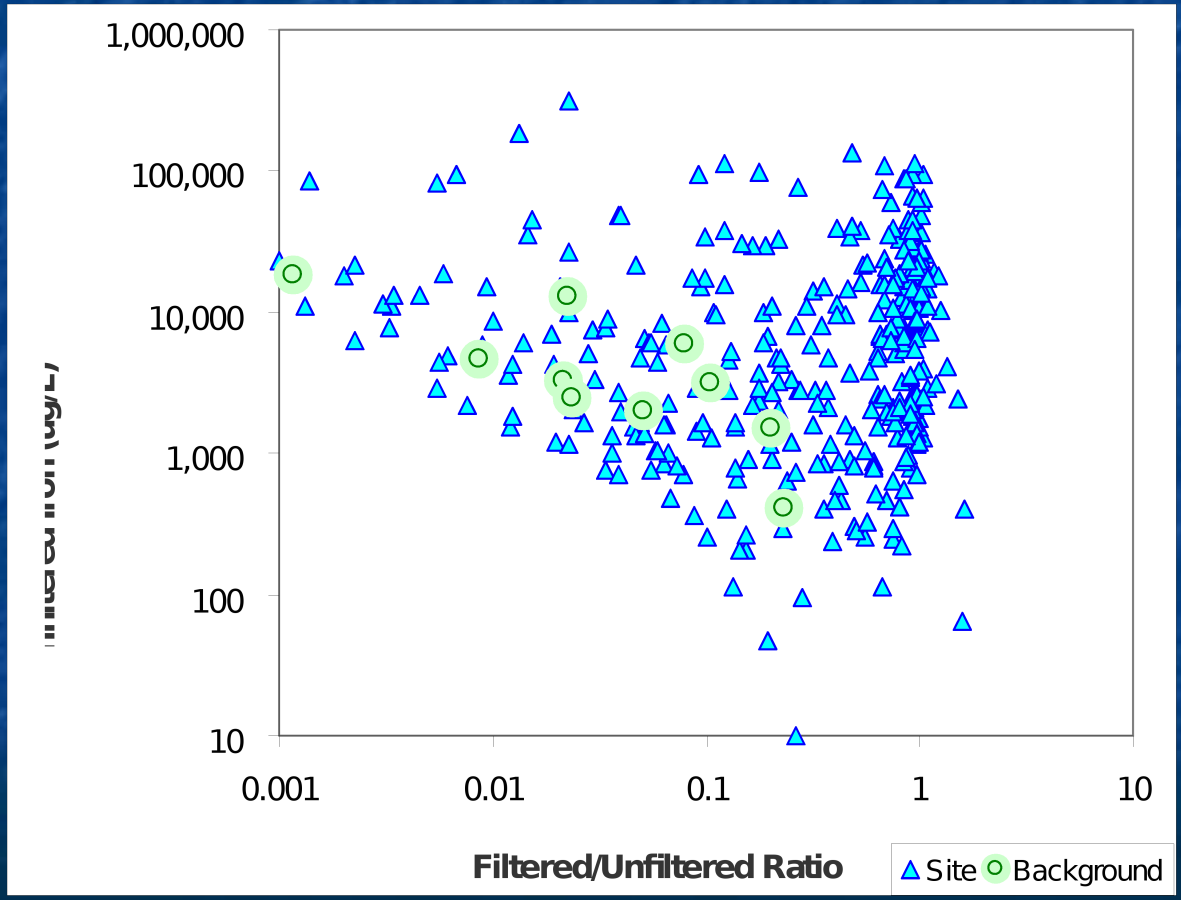
ORP: -421 to +344 mV

mean = -31 mV

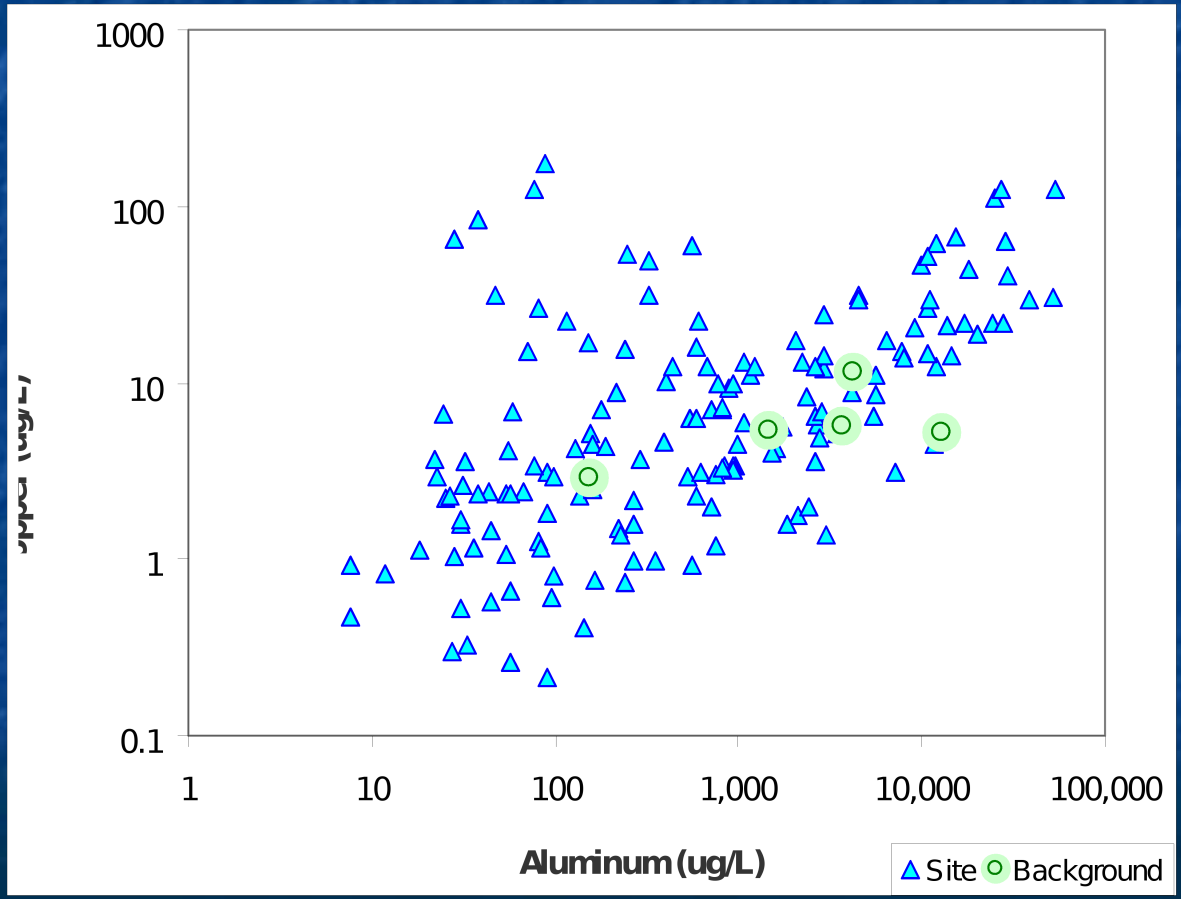
Site 5 (Virginia): Unfiltered Aluminum vs. Filtered/Unfiltered Ratio



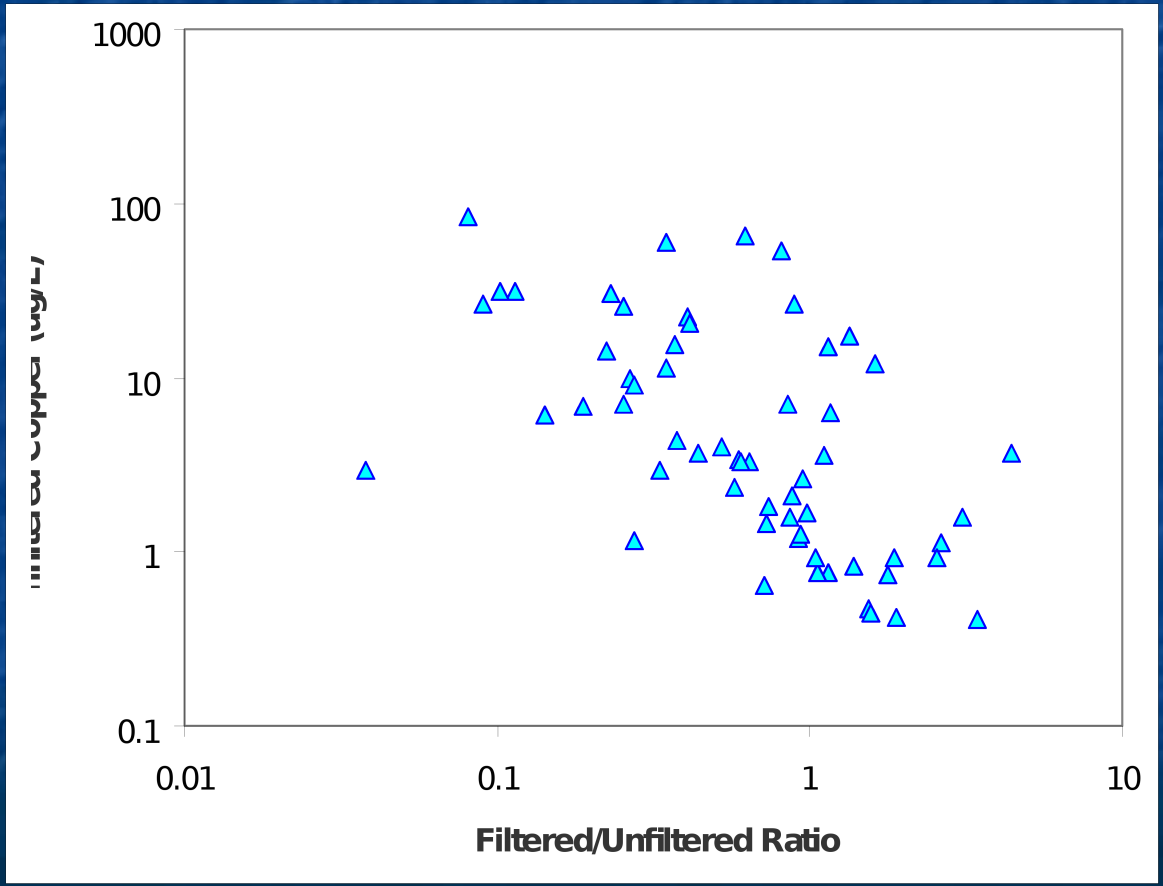
Site 5 (Virginia): Unfiltered Iron vs. Filtered/Unfiltered Ratio



Site 5 (Virginia): Copper vs. Aluminum in Unfiltered Groundwater



Site 5 (Virginia): Unfiltered Copper vs. Filtered/Unfiltered Ratio



Conclusions

- Geochemical evaluation is a cost-effective approach for determining if metals contamination of groundwater has occurred

  Uses existing data (requires Al, Fe, Mn analyses)

  Does not require a valid background data set

  Lowers the probability of a false-positive determination

  Identifies the mechanism(s) responsible for elevated metals concentrations

- Geochemical evaluation complements statistical site-to-background comparisons

  If an element in the site data set fails a statistical test, then a geochemical evaluation should be performed